The electronic structure of amorphous silica:
A numerical study

Thorsten Koslowski[1], Walter Kob[2] and Katharina Vollmayr[3]

[1] Institut für Physikalische Chemie und Elektrochemie I,
Universität Karlsruhe, Kaiserstraße 12,
D-76128 Karlsruhe, Germany

[2] Institut für Physik, Johannes-Gutenberg-Universität,
Staudinger Weg 7, D-55099 Mainz, Germany

[3] Institute for Physical Sciences and Technology,
University of Maryland, College Park, MD 20742, USA

Abstract

We present a computational study of the electronic properties of amorphous SiO_2. The ionic configurations used are the ones generated by an earlier molecular dynamics simulations in which the system was cooled with different cooling rates from the liquid state to a glass, thus giving access to glass-like configurations with different degrees of disorder [Phys. Rev. B **54**, 15808 (1996)]. The electronic structure is described by a tight-binding Hamiltonian. We study the influence of the degree of disorder on the density of states, the localization properties, the optical absorption, the nature of defects within the mobility gap, and on the fluctuations of the Madelung potential, where the disorder manifests itself most prominently. The experimentally observed mismatch between a photoconductivity threshold of 9 eV and the onset of the optical absorption around 7 eV is interpreted by the picture of eigenstates localized by potential energy fluctuations in a mobility gap of $\sim$9 eV and a density of states that exhibits valence and conduction band tails which are, even in the absence of defects, deeply located within the former band gap.

1. Introduction

Apart from being of great importance in chemistry, optics, geology and industrial applications, silica is a prototype of a strong glass former and has thus been investigated extensively by experimental, theoretical and computational techniques. It is generally believed that a-SiO_2 shares its microscopic structure with the low-density crystalline phases of SiO_2 and that bond lengths and bond angles show values comparable to their crystalline counterparts. The concept of a random network of corner-sharing tetrahedral SiO_4 units has been postulated as early as 1932 by Zachariasen to describe the microscopic structure of a-SiO_2 [1]. Apart from the construction of random networks – either by hand or by computer – it is today also possible to study relatively large models of a-SiO_2 which have been generated by means of a molecular dynamics computer simulation in which the sample was quenched with a cooling rate that is small compared to the inverse of the time scale characteristic for atomic motion in fluids at elevated temperatures [2, 3].

Whereas there are numerous calculations of the electronic structure of the crystalline phases of SiO_2, including recent self-consistent computations within the local density approximation [4, 5], information on amorphous SiO_2 is sparse. Early work – usually based on local molecular orbital schemes – has, e.g., been reviewed by Griscom [6]. Laughin *et al.* have presented a tight-binding study of a-SiO_2 on a Bethe lattice and compared it to α-quartz [7]. Gupta [8] has used a tight-binding approach to compare the electronic structure of α-quartz to a continuous random network (CRN) geometry constructed by Dean and Bell [9] containing 614 atoms and a structure generated by a molecular dynamics (MD) simulation of rapid quenching, containing 648 atoms [10]. Recently, Ordegon and Yndurain have presented computations on both crystalline [11] and amorphous [12] modifications of SiO_2. In these calculations, matrix elements obtained from Hartree-Fock calculations for small clusters have been transferred to a Bethe lattice, the density of states has been obtained within a Green's function approach. Compositional disorder was handled within an effective medium theory.

In the present work, we address the question of the electronic structure of models of amorphous SiO_2 generated by molecular dynamics simulations.

The electronic structure is described by a simple tight-binding Hamiltonian, including the crucial component of a fluctuating Coulombic site energy, which to our knowledge has been neglected in all previous approaches. We focus on the computation of this fluctuation in the potential energy as a function of the cooling rate with which the geometry was produced and its influence on the density of states, the localization properties of eigenstates around the former band gap and an approximate computation of the onset of the optical absorption spectrum.

The rest of this article is organized as follows: In the next section we briefly outline the generation of the atomic configurations and give a detailed description of the tight-binding electronic structure calculation and its subsequent analysis. In the third section, results are presented and discussed in comparison with experiments. Conclusions are gived in the last section.

2. Methods

The configurations of the ions used as input for the present electronic structure calculations are the ones generated recently by Vollmayr *el al.* in a molecular dynamics simulation of SiO_2 [2, 3]. The potential used was the one proposed by van Beest *et al.* (BKS) [13], which has been demonstrated to give a good description of the various crystalline phases of silica [14]. The BKS potential contains only two-body interactions and reads

$$V(r_{ij}) = \frac{e^2}{4\pi\epsilon_0}\frac{z_i z_j}{r_{ij}} + A_{ij}\exp(-B_{ij}r_{ij}) - \frac{C_{ij}}{r_{ij}^6} \quad . \tag{1}$$

The values of the different parameters can be found in Refs. [3, 13]. For the computation of the electronic structure presented here it is important to note that partial charges of $z_+=z_{Si}=2.4$ and $z_-=z_O = -1.2$ have been used. Furthermore we note that in the work of Vollmayr *et al.*, as well as in the present work, the non-Coulombic part of the potential was truncated and shifted at a distance of 5.5Å. This truncation has the effect that the density of the amorphous configurations is in agreement with the experimental value of silica glass.

The goal of the work of Vollmayr *et al.* was to investigate how the structural properties of silica depend on the rate with which the sample was quenched, at constant pressure, from the liquid state at high temperatures to an amorphous state at low temperatures. For this the system was equilibrated at a high temperature $T_i = 7000$ K and subsequently coupled to a stochastic heat bath with temperature $T_b(t)$. The temperature of this heat bath was decreased linearly in time, i.e. $T_b(t) = T_i - \gamma t$, where γ is the cooling rate. After T_b reached 0 K, the so obtained configurations were relaxed with a steepest descent method and subsequently analyzed. By varying the cooling rate over more than two decades ($\gamma = 1.1 \cdot 10^{15}$ K/s, $5.7 \cdot 10^{14}$ K/s, $2.8 \cdot 10^{14}$ K/s, $1.4 \cdot 10^{14}$ K/s, $7.1 \cdot 10^{13}$ K/s, $3.6 \cdot 10^{13}$ K/s, $1.8 \cdot 10^{13}$ K/s, $8.9 \cdot 10^{12}$ K/s and $4.4 \cdot 10^{12}$ K/s) it was possible to investigate how the properties of the glass, such as various bond lengths or the distribution of the bonding angles, depend on the cooling rate. In order to improve the statistics of the results an average over ten independent runs was made for each value of γ. At the beginning of the next section we will give a brief summary of those results in order to facilitate the interpretation of the results of the present electronic structure calculation. Details of the cooling rate simulation can be found in Ref. [3].

The electronic structure is described by a tight-binding Hamiltonian

$$H = \sum_{ia} \epsilon_{ia} c_{ia}^\dagger c_{ia} + \sum_{i \neq j, ab} t_{ijab} c_{ia}^\dagger c_{jb} \qquad (2)$$

with creation/annihilation operators acting upon atomic orbitals indexed a, b centered at atoms i, j. A basis set of one s and three p orbitals has been used for both silicon and oxygen atoms. We use the diagonal and off-diagonal parameters ϵ^0 given by Robertson [15]: the differences between the diagonal energies $\epsilon_{Si,s}^0 = 5.1$ eV, $\epsilon_{Si,p}^0 = 11.1$ eV, $\epsilon_{O,s}^0 = -16.0$ eV and $\epsilon_{O,p}^0 = -1.08$ eV almost coincide with those of the valence orbital ionization potentials [16]. Hopping matrix elements t_{ijab} exist between neighbor Si and O atoms. In addition, hopping between two oxygen atoms bonded to the same Si atom is allowed. For Si-O bonds, matrix elements are generated using $V_{ss\sigma} = -3.0$ eV, $V_{sp\sigma} = 5.2$ eV, $V_{pp\sigma} = 6.0$ eV and $V_{pp\pi} = -1.0$ eV; the only nonzero hopping matrix elements for O-O bonds are $V_{pp\sigma} = 0.56$ eV and $V_{pp\pi} = -0.13$ eV. Matrix elements between atomic orbitals depend on the direction cosines and are modified according to the Slater-Koster rules [17]. Neighborhoods are defined

5

by two cutoff radii, we use r_1=2.2 Å for nearest and r_2=3.0 Å for next-nearest neighbors, in accord with the definition of neighborhoods in the analysis of the microscopic structure of the same geometries [3].

As will be elaborated below, in disordered systems with a strong ionic character, the Madelung potential – and thus the diagonal of the Hamiltonian matrix – depends on the center-of-mass coordinates due to the underlying disorder. As we believe the average on-site energies to be well represented by the parametrization scheme described above, we consider fluctuations around these averages via

$$\epsilon_{ia} = \epsilon_{ia}^0 + \langle V_M \rangle_i - \frac{e^2}{4\pi\epsilon_0} \sum_{j \neq i} \frac{z_j}{r_{ij}} \quad . \tag{3}$$

Here V_M is the Madelung potential, the last term on the right hand side. We would like to note that we define the Madelung potential entering the Hamiltonian (2) using an electronic test charge placed at site i. The resulting large eigenvalue/eigenvector problems of the size of 4008 basis functions have been solved using storage-efficient Lanczos algorithms [18].

The localized or extended nature of eigenstates within the former crystalline band gap decides the size of the mobility gap. As a measure of electron localization, we use the modified inverse participation ratio (MIPR). For normalized eigenstates $|\alpha\rangle$, it is given by

$$\text{MIPR} = n^{1/2} \sum_i a_{i\alpha}^4, \tag{4}$$

where $a_{i\alpha}$ are the expansion coefficients of the eigenstates $|\alpha\rangle = \sum_i a_{i\alpha}|i\rangle$. The MIPR is related to the inverse participation ratio, from which it differs by the factor of the square root of the number of particles. The participation ratio, $n^{1/2}/\text{MIPR}$, is a rough measure of the number of atomic orbitals over which an eigenstate is extended. The scale invariance of the MIPR at the point of the transition from localized to extended eigenfunctions has been attested by Chang et al. [19]. For a variety of systems, an MIPR value close to unity separates localized from extended states and thus marks the mobility edge [20].

Being interested in the contribution of different types of atomic orbitals or of defects to eigenstates, we have performed a population analysis. The

Mulliken charge order

$$q_\alpha = \sum_i{}' \langle\alpha|i\rangle\langle i|\alpha\rangle = \sum_i{}' a_{i\alpha}^2 \tag{5}$$

serves as a measure of the participation of a specific type of orbitals – hence the restriction of the sum indicated by a prime – in an eigenfunction $|\alpha\rangle$ [21]. In the thermodynamic limit, the product of the charge order and the density of the states equals the partial density of states (PDOS).

3. Results and discussion

3.1 Microscopic structure

In this subsection we briefly summarize some of the results of the work of Vollmayr *et al.* [2, 3] in order to facilitate the understanding of the results of the present electronic structure calculations.

As already mentioned in Sec. 2, the goal of that work was to investigate how various properties of the glass depend on the cooling rate γ with which the glass was quenched from the liquid state. Regarding the structural properties it was found that the peaks in the various radial distribution functions, or in the partial structure factors, become more pronounced with decreasing γ. In particular it was shown that the so-called first sharp diffraction peak in the structure factor increases significantly, which shows that the arrangement of the ions become more ordered not only locally, i.e. on the length scale of one Si-O bond, but also on the intermediate range length scale, i.e. on the length scale of a few tetrahedra. This observation was corroborated by the fact that also the distribution of the various bond angles, such as the intra-tetrahedral angle O-Si-O, or the inter-tetrahedral angles Si-O-Si and Si-Si-Si showed significantly more pronounced peaks with decreasing cooling rate. Furthermore it was found that the distribution of the rings of a given size depends strongly on the cooling rate in that with decreasing γ the frequency of very short rings ($n \leq 3$), as well as the ones of the long ones ($n \geq 8$), decreases. Here n is the number of Si-O pairs in a ring. On the other side the frequency of rings with length $n = 5$ and 6 increases with decreasing cooling

rate, which can be understood by remembering that at normal pressures the crystalline phase of silica, β-crystobalite, purely consists of six-membered rings. Thus it is reasonable to assume that with decreasing cooling rate the *local* structure of the glass is quite similar to the one of β-crystobalite.

3.2 Madelung potential fluctuations

Potential energy fluctuations play a crucial role in the understanding of electronic properties of ionic liquids. Due to the disorder in the positions of the ionic centers of mass, the Madelung potential V_M is not a constant as in an ideal crystalline system, but a function of the ionic coordinates. This concept has been introduced by Logan and Siringo [22] to ionic fluids. These authors have used the mean spherical approximation (MSA) to compute the fluctuations ΔV_M of V_M for the restricted primitive model at high density, as relevant for molten CsAu. At the melting point of simple ionic systems, ΔV_M is of the order of one electron Volt; linear graphic theories of liquids like the MSA predict a Gaussian distribution of potential energies [22]. The impact of a random Madelung potential upon the electronic structure of fluids has been studied numerically for liquid $Cs_x[CsAu]_{1-x}$ [23], molten alkali halides like KCl [24], alkali halide - alkali metal solutions $K_x[KCl]_{1-x}$ [25] and liquid silver chalcogenides [26].

Having generated SiO_2 geometries by molecular dynamics simulations we are able to address the question whether these fluctuations persist once a fluid is rapidly quenched into the amorphous state. Using an electronic test charge and full formal charges $z_+=4$ and $z_- = -2$, we have computed the anionic and cationic Madelung potentials and their fluctuations. In Fig. 1 we show ΔV_M as a function of the cooling rate γ. We recognize that the Madelung potential fluctuations are increasing with increasing γ and that they are on the order of $\sim$1.75 eV for the fastest and $\sim$1 eV for the slowest cooling rate studied. In general, fluctuations in the anionic Madelung potential are stronger than those in their cationic counterpart, a tendency that seems to increase with increasing cooling rate. Compared to fluids at elevated temperatures [27], fluctuations in ΔV_M for quenched SiO_2 from one realization to the other are surprisingly large, the corresponding RMS deviation is of the order of 0.15 eV,

as depicted by the error bar Fig. 1 for the cationic ΔV_M with the largest value of γ. Even with the large amount of data used in this study we see no way of performing a reliable extrapolation to a cooling rate which is typical in a real experiment. Any reduction of the formal charge z_1 to an effective charge z_2 will reduce the potential energy fluctuations accordingly, since the RMS deviations obey the relation $\Delta V_M(z_1)/\Delta V_M(z_2) = z_1/z_2$. Thus any possible reduction of the Coulombic site energy fluctuations by a slower quenching procedure can be partly compensated by using the full formal charge – the customary procedure when one computes Madelung potentials – instead of the simulation charge as frequently done in this work.

3.3 Density of states

To discuss the influence of topological disorder, bond angle fluctuations and Madelung potential fluctuations upon the density of states, we use the crystalline DOS – as computed by Robertson [15] using the same set of parameters as in that work – which is shown in Fig. 2a as a reference. The tight-binding parameters are chosen to make the upper edge of the valence band the zero of energy. The narrow band around –18 eV is dominated by oxygen 2s orbitals, a structured valence band of width $\sim$13 eV is separated from the conduction band by a band gap of $\sim$9 eV, in good agreement with the experimental value of the conductivity gap of $\sim$9.4 eV in α-quartz [28]. States at the top of the valence band display a strong contribution of oxygen 2p orbitals and exhibit a nonbonding character. Details of the models of a-SiO$_2$ used for electronic structure computations in this work are also listed in table 1.

As mentioned in Sec. 3.1, in our system the disorder manifests itself in the distribution of bond lengths, bond angles and in the possible deviation of the size of $(SiO)_n$ rings from those observed in crystalline systems, including the presence of odd-membered rings. In a computer experiment, it is straightforward to study the influence of the disorder on the density of state even if the fluctuations in the Madelung potential are absent and in Fig. 2 we present the result of such a calculation.

For the smallest cooling rate (γ=4.4·10^{12} K/s), the resulting density of states

is displayed in Fig. 2b. In contrast to the alkali halides [24], the main features of the bands are remarkably persistent with respect to the introduction of disorder. Whereas the fine structure of all bands is smoothed out considerably, usually attributed to the breakdown of topological disorder [29], a significant broadening of the bands can only be found at the bottom of the valence band, the bottom of the oxygen 2s band and at the top of the conduction band. For the energies at which changes in the density of states have the most profound physical influence – in the gap around the Fermi level – no tailing can be observed within the resolution of the DOS as presented here (0.25 eV). A small number of eigenstates (two out of 40080 for γ=4.4·10^{12} K/s and ten for γ=1.1·10^{15} K/s) have been found at energies around 3-4 eV. Inspecting the corresponding eigenvectors, these states can be unambiguously attributed to the highest occupied orbitals of four-membered $(SiO)_2$ rings.

This situation changes considerably once Madelung potential fluctuations are introduced (Fig. 2c). Using the full formal charges z_{Si}=+4 and z_O=–2 on the ions, we observe a considerable tailing of both the upper valence band edge and the lower conduction band edge into the former band gap. The amount of band tailing evidently depends on the cooling rate and thus on the thermal history of the model system: the solid line corresponds to a cooling rate of γ=4.4·10^{12} K/s, as in Fig. 2b, the dotted line to a γ value of 1.1·10^{15} K/s. The question of the localized or extended nature of states in the gap – crucial for the existence and the size of a mobility gap – will be addressed in the next section.

3.4 Localization properties and the mobility gap

As stated above, in this work the modified inverse participation ratio [MIPR, Eq. (4)] serves as a measure to determine whether the nature of eigenstates around the Fermi energy is localized or extended. With a system size restricted to 1002 atoms, we did not study the dependence of localization measures upon the system size, but took a MIPR value larger than unity as an indicator of localized states, and a MIPR value smaller than unity characterizing extended states. As will be shown below, the crossover between localized and extended states is sharp for the large systems studied here, so

10

the error made for the size of the mobility gap resulting from small deviations of the critical MIPR from the value of unity should be small.

The MIPR as a function of energy is presented in Fig. 3. With Madelung potential fluctuations switched off (γ=4.4·10^{12} K/s, ∇) we observe the following localization behavior: At the bottom of the conduction band, only extended states exist. This is a clear numerical verification of the hypothesis that neither bond angle nor topological disorder are sufficient to induce localization within an energy interval larger than some tenths of an electron volt for eigenstates with a strongly bonding character [30]. At the top of the nonbonding oxygen band, a crossover from extended to localized states can be observed. It is, however, important to note that only two out of 40080 eigenstates lie in the energy interval at the top of the valence band. Thus we see that in the absence of Madelung potential fluctuations, localized eigenstates dominate an energy interval of some tenths of an electron Volt at the top of the valence band, that their total number is, however, negligibly small. The mobility gap and the energy interval containing no density of states almost coincide.

In the presence of Madelung potential fluctuations, the situation is changed dramatically. For the same cooling rate of γ=4.4·10^{12} K/s ($\times$) as before, the MIPR crosses its critical value of unity both at the top of the valence and at the bottom of the conduction band, a broad range of localized eigenstates appear in the former band gap. The size of the mobility gap is approximated as ~9.1 eV. The most localized states deep in the gap are extended over little more than an oxygen atom, thus are close to the maximum degree of localization. If the amount of disorder present in the structure is increased, by increasing the cooling rate to 1.1·10^{15} K/s ($\circ$,solid line), no qualitative change of the energy dependence of the MIPR is observed, albeit the statistics has improved, due to the larger number of eigenstates in the former gap (cf. Fig. 2c). The magnitude of the mobility gap increases slightly.

To summarize, Madelung potential fluctuations provide the only mechanism for the creation of eigenstates deep in the former gap within the model systems studied here. The size of the mobility gap dominated by localized states is of the order of 9 eV, close to the experimental crystalline conductivity gap of 9.4 eV (α-quartz), the onset of photoconductivity in a-SiO$_2$ with an upper

11

boundary of 9.0 eV [31], and the photoinjection threshold of 8.9±0.2 eV, which is not sensitive to selection rules [31].

3.5 Band tails and the optical gap

The experimentally observed photoconductivity of a-SiO$_2$ of 9.0 eV is thus consistent with two types of the density states presented in this work: i) in the absence of Madelung potential fluctuations (Fig. 2b, Fig. 3, ∇ symbol) the mobility gap almost coincides with the band gap, topological disorder does neither lead to a significant band tailing nor to localization at the band edges; or ii) in the presence of Madelung potential fluctuations, localized eigenstates exist deep within the former band gap (Fig. 2c, Fig. 3, $\circ$ and $\times$ symbols), and the onset of the photoconductivity originates from a large mobility gap of ~ 9 eV. In this section, we will investigate whether one of the two pictures has to be abandoned if the optical absorption properties of a-Si are considered.

The imaginary part of the dielectric function, ϵ_2, governing the optical absorption, can be approximated by the joint density of states, JDOS, divided by the excitation frequency [32]:

$$\epsilon_2(\omega) \propto \omega^{-1} \int_{-\infty}^{E_F} \text{DOS}_{VB}(E)\text{DOS}_{CB}(E + \hbar\omega)dE, \qquad (6)$$

where DOS_{VB} and DOS_{CB} denote the valence and the conduction band density of states. This approach neglects variations of the dipole transition matrix element with energy, an approximation considered to be particularly severe in the case of SiO$_2$ [33]. In the present work, however, our primary concern is the shape of the absorption edge originating from eigenstates that can be located within the former crystalline band gap. In this energy range, the JDOS will vary over several orders of magnitude. Variations in the dipole transition matrix element will be comparatively small since due to the random nature of the model systems, there exist no transitions that is strictly forbidden by symmetry. The first optical band in crystalline SiO$_2$ is usually attributed to an exciton at 10.4 eV [34]. The experimental determination of the indirect band gap is thus restricted to the measurement of the photo-

conductivity. The first clear peak of the optical absorption spectrum can be observed at 11.7 eV [35].

The geometries obtained from MD simulations still contain a small number of defects, which may spoil the comparison of the computed absorption to experiments with those samples of amorphous SiO_2 where defects are believed to be removed by the addition of water [36]. As the band tailing is primarily caused by Madelung potential fluctuations, we simply superimpose potential energy fluctuations obeying a Gaussian distribution on a model system with the geometry of α-crystobalite. To compute a property originating from an integration over the DOS, 25 realizations of systems containing 638 atoms turn out to be sufficient. The resulting optical absorption is presented in Fig. 4. Absorption edges associated with systems exhibiting Madelung potential fluctuations show a significant tail, the onset and slope of which is determined by the RMS deviation of the Coulombic potential energy. With $\Delta V_M^+ = \Delta V_M^- = 0.6$ eV, corresponding to the use of the charges used within the MD simulations and a conservative estimate of the strength of potential energy fluctuations (see Sec. 3.2), the onset of the absorption can be located around 7 eV (∇), full formal charges give rise to an onset at 5.5 eV ($+$), and a reduction of the charge to half of the formal charge shifts the onset of the spectrum at 8 eV ($\times$). As all spectra show an exponential tail, there is no clear termination of the absorption spectra, the overall trend, however, is evident from Fig. 4. Removing the aforementioned defect states associated with the presence of four-membered rings, a band edge in the absence of Madelung potential fluctuations is also presented in Fig. 4 ($\circ$, $\gamma=4.4\cdot10^{12}$ K/s). An energy as high as 9 eV is required to induce a small absorption for a system exhibiting only bond angle and topological disorder.

The experimentally observed onset of the absorption spectrum crucially depends on the water content of the sample [36]: glasses characterized by a small concentration of water shows an absorption peak at 7.6 eV preceding a continuous absorption spectrum. The intensity of this maximum depends on the sample studied. No such peak is found for glasses characterized by a comparatively high concentration of water; again depending on the type of silica, the onset of the absorption spectrum can be located around 7.0 ± 0.2 eV [36]. The role of H_2O has been interpreted as saturating defects like dangling bonds and thus removing the corresponding eigenstates from the

band gap [31]. This interpretation encourages us to compare the absorption edges obtained from samples with a high concentration of water – moving defect states into the valence or conduction band by the formation of a strong chemical bond – to our model free of defects, which is governed by fluctuations of the Coulombic site energies. It is evident from Fig. 4 that Madelung potential fluctuations of 0.6 eV – as induced by the charges used in the pair potential Eq. (1) – are sufficient to shift the absorption edge to the red by two electron Volts, now coinciding with the experimental value.

It has to be noted that the precise form of the band edges computed via iterative schemes like the recursion method, depends on the way the continued fraction is terminated, so we see no way of getting around the laborious way of studying a large number of slowly quenched large systems or carefully equilibrated CRNs by exact diagonalization. Naturally, the same argument holds for the computation of localization properties of eigenstates within the pseudo-gap.

3.6 The role of defects

As stated in Sec. 3.3, only an extremely small fraction of defects associated with the presence of four-membered $(SiO)_2$ rings can be located within the former band gap, if the fluctuations of the Madelung potential are absent. To our knowledge, there is no experimental evidence either of these states or of small rings in amorphous silica. There is no connection between these states and any type of over- or under-coordinated silicon or oxygen atom. We believe that these rings will be suppressed by further decreasing the cooling rate and in Ref. [3] evidence was given for this.

Once Madelung potential fluctuations are introduced, the fraction of gap states localized on four-membered rings can be neglected compared to the strong tailing of states at the band edges. Computing the defect charge order – Eq. (5) with the sum restricted to orbitals localized on under- or over-coordinated atoms – we notice that these defect basis functions now make a major contribution to localized eigenstates: the total charge order of defects peaks at a value close to 1/2 at an energy of ∼6 eV, as shown in Fig. 5. As also evident from this figure, under-coordinated oxygen atoms dominate the

14

defect density of states. It is remarkable that Madelung potential fluctuations do not simply broaden a defect band within the gap, but seem to be essential for the presence of defect states. A possible explanation for this behavior may be given by the strong localization of eigenstates in a random potential, reducing the coupling of dangling bond orbitals to the rest of the system and thus preventing these states from being split into high energy CB and low energy VB states by forming strong covalent bonds.

Note that these computations were performed for systems characterized by a cooling rate of $1.1 \cdot 10^{15}$ K/s, the small number of eigenstates deep within the gap does not permit us to make any statement based on proper statistics for the slowest cooling rate of $4.4 \cdot 10^{12}$ K/s.

4. Conclusions

We have presented a numerical study of the electronic structure of models of amorphous silica. The geometries used have been generated with a molecular dynamics simulation in which the system was quenched with different cooling rates, thus had a variable amount of disorder. The electronic structure has been described by a tight-binding Hamiltonian incorporating fluctuations arising from the disordered ionic center-of-mass positions, leading to variations in the Coulombic site energies with an RMS deviation of the order of 0.6 eV for the charges used in the MD simulation and the smallest cooling rates applied.

The influence of disorder upon the density of states, localization properties and the size of the optical gap are studied and discussed. Madelung potential fluctuations lead to the formation of a mobility gap of the order of 9 eV around the Fermi level, which turns out to be insensitive to any physically reasonable variation of the amount of disorder present in the model. The size of this energy interval containing only localized states not contributing to electronic transport is in accord with the experimental value of the photoconductivity threshold (9 eV) and with photoinjection experiments (8.9±0.2 eV) [31].

15

In the absence of Madelung potential fluctuations, band tailing is suppressed, and the amount of localized states within the former gap is vanishingly small. This behavior would imply an optical gap of the order of 9 eV, whereas a-SiO$_2$ optimized for transparency in the UV region exhibits an onset of the optical absorption around 7 eV [36]. A defect-free model incorporating only site disorder – a simple model to mimic the removal of defect states from the gap by increasing the content of water – does, however, reproduce the numerical value of the gap, again using the charges applied within the MD simulations.

To conclude, fluctuations in the Madelung potential – a key element in the theory of the electronic structure of ionic fluids [22] – persist in models of quenched silica at least for cooling rates down to the order of 10^{12} K/s. This concept arising from liquid-state theory turns out to be crucial for the understanding of the nature of electronic eigenstates within the gap. It provides a possible mechanism to induce the strong mismatch of the mobility gap and the optical gap of 2 eV, as observed in a-SiO$_2$.

Acknowledgments

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Table 1

Models of quenched SiO_2 used for electronic structure calculations. All amorphous geometries originating from MD simulations contain 1002 atoms (10 realizations), lattice geometries contain 638 atoms (25 realizations).

Model index	Model geometry	ΔV_M^+ (eV)	ΔV_M^- (eV)	γ (K/s)	fig.2	fig.3	fig.4
1	amorphous	0.89	0.93	$4.4 \cdot 10^{12}$	c	$\times$	
2	amorphous	1.58	1.88	$1.1 \cdot 10^{15}$	c	$\circ$	
3	amorphous	zero	zero	$4.4 \cdot 10^{12}$	b	∇	$\circ$
4	amorphous	zero	zero	$1.1 \cdot 10^{15}$			
5	lattice	0.3	0.3	$-$			$\times$
6	lattice	0.6	0.6	$-$			∇
7	lattice	1.0	1.0	$-$			$+$

Figure captions

Figure 1 Cationic ($\circ$) and anionic ($\times$) Madelung potential fluctuations, ΔV_M, as a function of the logarithm of the cooling rate, γ. Solid and dotted lines are a guide to the eye.

Figure 2 Silica density of states for various degrees of disorder: a) crystalline α-quartz (after [15]), b) amorphous silica, $\gamma=4.4\cdot10^{12}$ K/s, without Madelung potential fluctuations, c) amorphous silica with Madelung potential fluctuations (solid line: $\gamma=4.4\cdot10^{12}$ K/s, dotted line: $\gamma=1.1\cdot10^{15}$ K/s).

Figure 3 Logarithm of the modified inverse participation ratio as a function of energy. ∇: $\gamma=4.4\cdot10^{12}$ K/s, no Madelung potential fluctuations; $\times$: $\gamma=4.4\cdot10^{12}$ K/s, including Madelung potential fluctuations; $\circ$: $\gamma=1.1\cdot10^{15}$ K/s, including Madelung potential fluctuations (solid line is a guide to the eye).

Figure 4 Logarithm of the joint density of states divided by the excitation frequency as a function of energy: +: lattice model, cationic charge $z_+=4$; ∇: lattice model, $z_+=2.4$; $\times$: lattice model, $z_+=1.2$; $\circ$: quenched SiO$_2$, $\gamma=4.4\cdot10^{12}$ K/s, no Madelung potential fluctuations. Solid and dotted lines are a guide to the eye.

Figure 5 Dimensionless defect charge order as a function of energy for $\gamma=1.1\cdot10^{15}$ K/s: total ($\circ$, solid line) and singly bonded oxygen charge order ($\times$, dotted line). Lines are a guide to the eye;